

FABRICATION AND CHARACTERIZATION OF MEDIUM DENSITY
FIBER BOARD PREPARED FROM ENZYME TREATED FIBER AND LIGNIN
BASED BIO ADHESIVE

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ABSTRACT

The emission of formaldehyde vapours from the adhesives such as urea formaldehyde (UF) and phenol formaldehyde (PF) is a serious concern associated with the wood composite industry. In this research a sequential and systematic application of laccase enzyme was applied to modify the rubberwood (*Hevea brasiliensis*) fibers and prepared an improved medium density fiberboard (MDF) without synthetic adhesive. The treated fiber was dried in an oven and stored in a desiccator whereas the solution obtained was called enzyme hydrolysis lignin (EHL) retained and concentrated until 3% solid content. The fiber properties were characterised by furrier transform infrared spectroscopy (FTIR), scanning electron microscope (SEM), thermo-gravimetric analysis (TGA) and x-ray diffraction (XRD). However the EHL and concentrated EHL were characterised by Brookfield viscometer, FTIR, DSC and TGA. Laccase treatment to fiber was optimised in order to obtain the best and improved fiber for MDF manufacturing. The best reaction parameters such as temperature, time, pH and enzyme amount, were investigated using response surface methodology. Crystallinity index was taken as response and maximum up to 10% increment was observed. The first approach included the laccase treatment to wood fiber in various amounts and reaction time in the pulp suspension. A successful binderless board were prepared from treated fibers at different platen temperature and at various pressing time. Water resistance properties and mechanical test such as MOE, MOR and IB of the boards were investigated. The binderless boards could not stand for longer time in water, whereas the mechanical properties were not strong enough to meet the international standard as per the ASTM D1037. Thus in order to improve the strength of MDF boards, another approach was applied and concentrated enzyme hydrolysis lignin (Con-EHL) was used as an adhesive. To evaluate the capability of Con-EHL as an adhesive, 6 mm MDF board of density 800 (± 10) kg/m³ was prepared from 5, 10 and 15% con EHL by weight of fiber and it was compared with standard UF based boards prepared using the same parameters. The prepared MDF boards exhibited a higher mechanical strength and meet the international standard but the board still cannot stand in the moisture resistance test. In the third approach, nine different combinations of soy-lignin based adhesives were prepared using different parameters such as pH and soy content. Physical and chemical properties of soy-lignin adhesives were investigated. It was observed that the MDF prepared by the alkali treated soy-lignin adhesives have improved physical and mechanical properties. Water absorption and thickness swelling was reduced in comparison to previous boards. Mechanical properties were comparable to the commercial grade MDF boards. In the fourth approach, the alkali based soy-lignin was further improved by increasing the soy content up to 20%, and treating it with different chemicals to improve the water resistance. The physical and mechanical properties of MDF were compared with commercial grade UF based MDF. Mechanical properties were found comparable to UF based MDF whereas thickness swelling and water absorption was observed better than the “C-series” of soy lignin adhesive. The present soy lignin based adhesive can be used as a replacement for the formaldehyde based adhesive. It will be more ecofriendly and less harmful for the health.

ABSTRAK

Pengeluaran wap formaldehid dari bahan pelekat seperti urea formaldehid (UF) dan fenol formaldehid (PF) menjadi kebimbangan yang serius dalam industri komposit kayu. Dalam kajian ini, enzim lakase telah digunakan untuk mengubahsuai serat kayu pokok getah (*Hevea brasiliensis*) dengan menggunakan aplikasi yang sistematik dan berjujukan serta menyediakan papan gentian berketumpatan sederhana (MDF) yang lebih baik iaitu tanpa bahan pelekat sintetik. Serat kayu yang dirawat dikeringkan di dalam oven dan kemudiannya disimpan di dalam baling pengering manakala cecair lignin enzim hidrolisis (EHL) yang diperoleh dikekalkan sehingga kandungan pepejal 3%. Sifat-sifat serat kayu tersebut dikaji dengan menggunakan spektroskopi inframerah transformasi furrier (FTIR), mikroskop electron imbasan (SEM), analisis gravimetri haba (TGA) and pembelauan x-ray (XRD). EHL dan EHL pekat pula dikaji dengan menggunakan meter kelikatan Brookfield, FTIR, kalorimetri pembesa imbasan (DSC) dan TGA. Rawatan lakase ke atas serat dioptimumkan untuk mendapatkan serat terbaik dalam pembuatan MDF. Parameter tindak balas terbaik seperti suhu, masa, pH dan jumlah enzim dikaji dengan menggunakan kaedah gerak balas permukaan. Indeks penghabluran telah diambilkira sebagai tindak balas dan kenaikan maksimum sehingga 10% diperhatikan. Pendekatan pertama meliputi rawatan lakase ke atas serat kayu dalam pelbagai jumlah dan masa tindak balas dalam penggantungan pulpa. Sekeping papan telah berjaya disediakan daripada serat kayu yang dirawat pada suhu plat dan masa menekan serat kayu yang berbeza. Ciri-ciri fizikal seperti rintangan air dan ciri-ciri mekanikal seperti MOE, MOR dan IB papan tersebut dikaji. Papan tersebut tidak boleh berada di dalam air dalam masa yang lama dan mempunyai ciri-ciri mekanikal yang tidak cukup kuat untuk memenuhi standard antarabangsa seperti ASTM D1037. Oleh itu, dalam usaha untuk meningkatkan kekuatan papan MDF, Satu lagi pendekatan telah digunakan dan Con-EHL telah digunakan sebagai bahan pelekat. Untuk menilai keupayaan Con-EHL sebagai bahan pelekat, 6 mm MDF pada ketumpatan papan 800 (± 10) kg/m³ telah disediakan daripada 5, 10 dan 15% kepekatan EHL mengikut berat serat dan ia telah dibandingkan dengan papan berasaskan UF disediakan menggunakan parameter yang sama. Papan MDF mempamerkan kekuatan mekanikal yang tinggi dan memenuhi standard antarabangsa tetapi masih tidak dapat bertahan dengan ujian rintangan kelembapan. Dalam pendekatan ketiga, sembilan kombinasi yang berbeza bahan pelekat berasaskan lignin soya telah disediakan daripada pelbagai parameter seperti pH dan kandungan soya. Sifat-sifat fizikal dan kimia bahan pelekat soya lignin telah dikaji. Dalam pemerhatian yang telah dilakukan, MDF yang disediakan dengan menggunakan lignin soya yang dirawat dengan alkali telah meningkat ciri-ciri fizikal dan mekanikal. Penyerapan air dan pembengkakkan ketebalan telah dikurangkan berbanding dengan papan sebelumnya. Sifat-sifat mekanikal adalah setanding dengan papan MDF gred komersil. Dalam pendekatan yang keempat, alkali berasaskan lignin soya telah dipertingkatkan lagi dengan meningkatkan kandungan soya sehingga 20%, dan merawat dengan bahan kimia yang berbeza untuk meningkatkan rintangan air. Ciri-ciri fizikal dan mekanikal MDF dibandingkan dengan gred MDF berasaskan UF komersial. Ciri-ciri mekanikal didapati dengan membandingkan asas UF di mana pembengkakkan ketebalan dan penyerapan air diperhatikan jauh lebih baik daripada bahan yang sebelumnya iaitu bahan pelekat soya lignin. Bahan pelekat lignin soya boleh digunakan untuk menggantikan formaldehid. Ia akan menjadi keluaran yang tidak mencemarkan alam sekitar dan kurang berbahaya untuk kesihatan.

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LIST OF SYMBOLS/ABBREVIATIONS

A	Absorbance
ANSI	American National Standards Institute
ASTM	American Society for Testing and Materials
CCD	Central Composite Design
cm	Centimeter
Con EHL	Concentration-EHL
DSC	Differential scanning calorimetry
EHL	Enzymatic hydrolysis lignin
FE-SEM	Field emission scanning electron microscope
FFD	Fractional Factorial Design
FTIR	Fourier Transform Infrared Spectroscopy
g	Gram
h	Hour
kg	Kilogram
l	Liter
m	Meter
M	Mole
Min.	Minute
ml	Milliliter
mm	Millimeter
mPa	MiliPascal
MPa	Megapascal

N	Newton
°C	Degree Celsius
PF	Phenol Formaldehyde
SEM	scanning electron microscope
TGA	Thermo-gravimetric analysis
UF	Urea Formaldehyde
V_{MDF}	MDF volume
XRD	X-ray Diffraction
ρ_{MDF}	MDF density

CHAPTER 1

INTRODUCTION

1.1 INTRODUCTION

Wood is the best example of a natural composite where mechanically strong cellulose fibers are oriented in a film of hemicelluloses and surrounded by a matrix of lignin (Winandy and Rowell, 2005). Since the start of civilization wood has been the most widely used building material. Due to the environmental concern and increasing demand from growing population, it is impossible to supply wood for present and future generation. Wood composite has emerged as an alternative for wood from the 20th century, where small logs, non-commercial timber, woodchips, shavings, and sawdust can be utilized to prepare a wood like structure (Isroi et al., 2011). With the increasing demand of wood composite, it is sure that future of wood industries will certainly depend on engineered wood product. Wood composite exhibits many advantages over solid wood like, smoothness, uniform structure, knots free surface, dimensionally stable, availability in different sizes and thickness, resistance to corrosion and fire, with a good tensile strength and easier to work (Hsu et al., 1989).

Composite wood panel products are made from wood-based materials bonded together with a synthetic adhesive using heat and pressure (Li et al., 2007). The wood materials include veneer, strands, particles, chips and fibers whereas adhesives are most commonly urea formaldehyde or phenol formaldehyde. Wood-based panel products have become increasingly specialized in recent years and are used in a wide range of applications. There are various wood based composites such as plywood, oriented strand board (OSB), particle board and medium density fiberboard available in the

market. The composite wood panels have been expanding into hybrid products also which combine two or more panels, or panels with other materials, into a single product. Wood based panels are an important sector, accounting for 9 %, (€13 000 million) of total industry production, employing around 80 000 people in the Europe (European Panels Federation, 2004). Total production of wood composite was estimated to be 45.6 million m³, in the year 2005. The construction and furniture market is the most important end-user for wood composite, followed by packaging. The furniture industry is the most important user of particleboard and MDF. Laminate flooring is a booming market for MDF and now accounts for nearly more than 40% of all applications (European Panels Federation, 2004).

Wood adhesives are essential components in wood composites. As the demand of wood composites are increasing, especially MDF market, there is greater demand of adhesives to convert low value wood to high quality and useful products. At present, formaldehyde-based synthetic adhesives such as phenol-formaldehyde (PF) and urea-formaldehyde (UF) resins are predominantly used (Kim et al., 2006). These adhesives are synthetically produced from non-renewable resources such as petroleum and natural gas (Moubarik et al., 2010a). The major drawbacks of formaldehyde-based resins are they emit formaldehyde which is harmful to human health (Li et al., 2009). Agency for Research on Cancer has classified it as a carcinogenic to human (IARC 2004). Furthermore, the decreasing petroleum resources and increasing price of fossil fuel has been a concern to the future cost and continues supply of synthetic adhesives (Imam et al., 2001). Number of research has been done to reduce or replace formaldehyde contents in adhesive preparation but none of them is commercially applicable till now (Mozaffar et al., 2004; Khan and Ashraf, 2006).

Due to environment concern and to maintain continues supply of adhesive, bio-based adhesives are a growing interest among researchers. Number of natural products like tannin, lignin, and more recently proteins based adhesives are under intense study to produce a bio-based natural adhesive (Pizzi, 2006; Mansouri et al., 2010). Since tannin and lignin both are polymer of phenol compound, they are primarily viewed as substituting option for synthetic phenolic resins. Tannin based adhesives have received more improvement and it is being used commercially for the last 20 years in southern

hemisphere of the world (Pizzi, 2003a). A huge availability of lignin as a by product of pulp and paper mills has made it an attractive raw material for adhesives (Pizzi, 2003b). In the past few decades number of patents has been done dealing with the application of pulp lignin as a wood adhesive, where lignin is cross-linked by condensation reactions (Nimz, 1983). The commercial use of lignin is still growing but the progress is very slow (Pizzi, 2006). A variety of protein has been suggested for protein based adhesive however, soy protein is the most popular among all due to its abundant and inexpensive availability worldwide. Soy based adhesive was first reported in 1920s but shortly after World War II, it was substituted by petroleum-based adhesives because of their improved adhesion and water resistance. Selection of protein as an adhesive is based on its functional properties such as solubility, gelation, viscosity, and emulsion stability (Wolf, 1970). A part of their intrinsic property all the proteins are desired to modify to improve its functional property through physical, chemical or enzymatic means.

Although, no of research have been done to utilized lignin as an adhesive but none of them is commercially viable. Thus, in order to improve the performance of lignin, an enzyme treatment technique has given a hope to prepare an eco-friendly board from lignin based adhesive. A variety of enzymes are available for the surface modification of ligno-cellulosic fibers (Chandra et al., 2004). Compared to chemical treatments which involve harsh reaction conditions and potential use of hazardous chemicals, enzymatic treatment conditions are often milder, less damaging to the fiber, and are environmentally friendly (Kunamneni et al., 2008). Enzymatic surface modifications of fibers can be accomplished with glucohydrolysis and oxidative enzymes. One of these oxidoreductases is laccase (benzenediol:oxygen oxidoreductase) which is a multi-copper-containing oxidoreductase enzyme widely distributed in plants and fungi (Milstein et al., 1989). The majority of fungi that produce laccase belong to the class of white rot fungi involved in lignin degradation and can mineralize this substrate (Ohkuma et al., 2001). Laccase can catalyze the oxidation of various substrates including phenols, diphenols, aminophenols, polyphenols, polyamines, and lignin related molecules, with concomitant reduction of oxygen to water.

The use of laccase enzymes to improve the bonding between pulp fibers has been applied frequently compared to other oxidoreductase enzymes (Felby et al., 1997,

(Lund and Felby, 2001; Mattinen et al., 2008). The treatments usually involve the application of laccase enzymes to activate lignin on fibers (one-component system) or the addition of another component with laccase to act as a potential cross-linking agent (two component system) (Gochev and Krastanov, 2007). Because laccase enzymes are too large to penetrate fibers (50-100 kDa) treatments should only result in a surface modification (Kunamneni et al., 2007). Therefore, during treatments of fibers to increase board strength, free phenolic groups on the fiber surface should act as potential reactive sites for laccase enzymes to create phenoxy radicals. Based on this theory, it is apparent that laccase can be employed to generate reactive quinonoid structures in lignin-rich fibers that could be reacted with amino acids to generate, enhanced fiber charge. This study examines the optimal grafting conditions with respect to fiber charge and its impact on sheet strength properties.

Obviously, there is an urgent need of a natural and low cost adhesive for a sustainable supply for wood composite products. Preparing a lignin based adhesive which is usually a waste of wood process is a very interesting concept. It would be highly desirable if adhesive is obtained from renewable resource while maintaining the mechanical strength and water resistance of the composite wood. A lot of work has been done to modify the lignin for adhesive purpose, but very few works has been done to use enzyme for lignin modification. It would be right time now, to make the wood composite industries an eco-friendly, self-sufficient with improved technology.

In addition to being eco-friendly, the composite materials of lignin-based adhesive will reduce the cost of production also as the chief raw material lignin, is a waste for pulp and paper process and available in huge quantity (Pizzy, 2003b). Since laccase has been recently commercialized and most abundant and cheaply available enzyme, it is further helping in reducing the cost of production. Owing to recent developments in the wood-composite market, it is apparently the most promising development in this field.